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(54) **Sealant composition.**

(57) A sealant composition for sealing punctures and/or ruptures comprises an alpha cyanoacrylate and powdered natural or synthetic rubber. A seal is made by applying the cyanoacrylate around the puncture and then spreading thereon a layer of rubber.

Description

SEALANT COMPOSITION

This invention relates to a sealant composition, more particularly to a cyanoacrylate-containing sealant composition useful to seal punctures and ruptures in various materials.

5 Sealant compositions have many uses. In some instances, for example for on-the-spot repair of car radiator or hose leaks, there is a need for the sealant to be easily and quickly applied and cured to repair the rupture. Various compositions advertised as sealants for such purposes have proved less than satisfactory. Even such products as the fast setting super glues, while excellent for adhering and gluing pieces together, have not been found suitable as sealants for the repair of ruptures, breaks and other types of openings in hoses, pipes, etc. Since the addition of activators and other materials which might have fast crosslinking and other hardening effects when incorporated within the cyanoacrylate would only serve to effect premature setting, this makes such additions highly impractical.

10 U.S. Patent No. 3,836,377 describes a method of priming a surface to improve its adhesion to alpha-cyanoacrylates, by treating the surface with compounds containing a group of formula:

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These dithiocarbamates, sulfenamides, etc., may also be incorporated directly into the cyanoacrylate to improve the cure.

25 U.S. patent no. 4,180,913 describes a dental material comprising an alpha-cyanoacrylate containing as filler a silica powder coated with a solid having a weak catalytic activity for the alpha-cyanoacrylate. After the composition is applied to the tooth, a "setter" composition comprising a basic amine compound having a strong catalytic activity to the alpha-cyanoacrylate is applied to cure the dental material. The curing promoters or "setters" are tertiary amines such as N,N-dimethyl-p-toluidine, N,N-dimethylaniline, etc.

30 U.S. patent no. 4,659,589 describes a process and composition involving the use of a powdered solid having hydroxyl and/or carboxylate groups therein to serve as an initiator or activator for a layer of an alkyl alpha-cyanoacrylate imposed over and around a rupture or an opening to be sealed. While the resultant seal is very effective and is rapidly formed, it is not as flexible as desired especially when formed on a material such as rubber.

35 We have now found that a very good sealant composition can be formed from two components, namely a first component comprising an alpha-cyanoacrylate in which the acrylate ester group has 1-10 carbon atoms, and a second component comprising as initiator or activator a powdered rubber which may be either a freshly vulcanized material or a reclaimed rubber. In use, the cyanoacrylate is applied to the rupture, etc., and to an area around the rupture, preferably after the surrounding surface has been cleaned and dried by wiping or by other suitable means. It is desirable to twist the material where possible to allow parting of the ruptured surfaces so that the cyanoacrylate may flow into the rupture and wet the surfaces thereof. After the 40 cyanoacrylate has been allowed to set for a very short period, sufficient of the solid activator is applied over the surface of the cyanoacrylate to cover the area above the rupture and the surrounding area.

45 Among the rubber materials which may be used are cis-1,4-polybutadiene, 1,2-polybutadiene, cis-1,4-polyisoprene, poly (chloroprene), butadiene-acrylonitrile copolymers, styrene-butadiene copolymers (both random and block copolymers), poly-(n-butylmethacrylate), and terpolymers of butadiene, acrylonitrile and acrylic acid. Powdered reclaimed rubber from used rubber products including tyres is also suitable.

One particularly suitable rubber material is a granular or ground reclaimed rubber from lorry and bus tyre tread, free of fabric and foreign material. This material usually has an approximate analysis of:

50 Acetone extractable 13-17%
Ash Content 5-7%
Carbon Black Content 29-33%
Moisture Content About 0.75%
Natural Rubber Content 20-30%
Rubber Hydrocarbon 29-45%
55 Typical bulk density 210 cc./100g.

Such a reclaimed powdered rubber material is available from Baker Rubber, Inc. of South Bend, Indiana, U.S.A. Three grades of varying particle size are:

TP-20

60 All passes through 16 mesh (USA Sieve)
30% Retained on 20 mesh
25% Retained on 30 mesh
72% Passes through 30 mesh

TP-30

All passes through 20 mesh (USA Sieve)

50% Retained on 30 mesh

25% Retained on 40 mesh

70% Passes through 40 mesh

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TP-40

All passes through 20 mesh (USA Sieve)

0.1% Retained on 30 mesh

10% Retained on 40 mesh

25% Retained on 50 mesh

64.9% Passes through 50 mesh

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While we do not wish to rely upon any particular mechanism or explanation of what reaction occurs during the hardening or sealing operation, it is believed that the rubber activator or initiator promotes a chain reaction at the surface of the cyanoacrylate layer, and that the chain reaction proceeds downwards through the thickness of the cyanoacrylate and causes hardening, possibly by further propagation of polymer molecules in the cyanoacrylate. In any case, the cyanoacrylate is hardened to effect the sealant function.

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The initiators which are useful in the practice of this invention to effect curing through the layer of cyanoacrylate by external application to the surface of the cyanoacrylate include a wide variety of rubber materials. Excess rubber material may subsequently be brushed away after the curing or hardening is completed. This rubber material may be diluted with an inert material, such as an inactive powder, provided the concentration of active material is sufficient to provide the desired curing activity.

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The alpha-cyanoacrylates useful in the practice of this invention are preferably liquid monomers having the formula $H_2C=C(CN)-COOR$ wherein R is an aliphatic, aromatic (preferably benzoid aromatic) or cycloaliphatic hydrocarbon group having from 1 to 10 carbon atoms, preferably alkyl, for example methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, pentyl, hexyl, heptyl, ethylhexyl, octyl, nonyl or decyl. From among these, it is particularly advantageous to employ those wherein R is alkyl having from 1 to 6 carbon atoms, either straight or branched chain. The aromatic and cycloaliphatic groups may have substituent groups, such as an alkyl having from 1 to 10 carbon atoms. The substituents are unlimited as long as the monomers are liquid. Illustrative substituents are lower alkoxy having from 1 to 4 carbon atoms [ethoxy-ethyl-alpha-cyanoacrylate] and halo, e.g. chloro and fluoro [trifluoro-isopropyl-alpha-cyanoacrylate]. In the trifluoro-isopropyl group, the three fluorine atoms are preferably bonded to the same carbon atom. In addition, R can also be, for example, cyclohexyl, methylcyclohexyl, phenyl, tolyl, chlorophenyl, propargyl, butynyl, butenyl or allyl. The sole restrictions on R are that the monomer must be liquid at room temperature (20° C) and atmospheric pressure and a carbon atom of R must be directly bound to the $H_2C=C(CN)-COO-$ group.

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These alpha-cyanoacrylate monomers can contain any of the other compounding ingredients which are normally employed, such as viscosity modifiers, coloring agents, fillers, pigments and the like.

Polymerization inhibitors such as sulfur dioxide may also be present. Instead of sulfur dioxide, other acidic inhibitors (against anionic polymerization) such as nitric oxide, nitrous oxide, carbon dioxide, p-toluene sulfonic acid, hydrogen fluoride, trichloroacetic acid and acetic anhydride, can be used to stabilize the monomer. Carbon dioxide is recommended only for monomers wherein R has at least four carbon atoms. In combination with the acidic inhibitor, a free radical inhibitor such as hydroquinone, monomethylether of hydroquinone, picric acid and t-butyl-catechol, pyrocatechol, p-methoxyphenol and the like, may be concurrently employed. The monomethylether of hydroquinone is the preferred stabilizer against free radical polymerization. Moreover, it imparts good color stability to both the monomeric alpha-cyanoacrylate and the polymerized product therefrom. Free radical inhibition may be obtained with about 10 parts of the monomethylether of hydroquinone per million parts of 1-cyanoacrylic acid ester: in practice from 15 to 200 parts per million are employed.

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The free radical polymerization inhibitor, like the anionic polymerization inhibitor, is normally added during the processing of the alpha-cyanoacrylate ester. Hence, a free radical polymerization inhibitor is generally introduced into the distillation vessel and the receiver to stabilize the ester in the synthesis thereof. As a result, commercially available alpha-cyanoacrylate esters may already contain a certain amount of a conventional free radical polymerization inhibitor such as those mentioned hereinabove.

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There may also be present in the adhesive compositions of this invention various other optional ingredients including, for example, plasticizers and thickeners. Plasticizers improve the ageing characteristics of the cured bonds by lessening the brittleness thereof. For the best performance, the amount of plasticizers to be used should not exceed 20% by weight of the total composition. Suitable plasticizers include monofunctional and difunctional aliphatic esters of acids having 1 to 10 carbon atoms such as, for example, dimethyl octyl sebacate and esters of malonic acid, difunctional aromatic esters, phosphates and phosphonates. Thickeners, which may be used in amounts of up to 25% by weight, depending in part on their degree of fluidity at room temperature, serve to increase the viscosity of the adhesives so that they may be more easily applied. Among the suitable thickeners for this purpose are for example polymeric alkyl alpha-cyanoacrylates, cellulose esters including cellulose acetate butyrate, acrylate resins such as poly(methyl methacrylate) and poly(ethyl methacrylate), and poly(vinyl alkyl ethers) such as poly(vinyl methyl ether).

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While as indicated above the flexibility of the cyanoacrylate cured layer is improved by using the rubber as the activator or initiator as described above, it has also been found that the rate of cure and toughness of the cured product are improved by using, with the rubber, one or more of the initiators or activators described in U.S. patent no. 4,659,589, namely a powdered solid having hydroxyl, carboxylate, or both hydroxyl and carboxylate groups therein. Typical of such powdered activators are mono and polysaccharides such as alginate, starch, pectin, carrageenan, locust bean gum, guar gum, cellulose, gum arabic, xanthate gum, sodium bicarbonate, polyvinylalcohol, a vinylalcohol-vinylacetate copolymer having at least 25% vinylalcohol groups therein, a sodium salt of polyacrylic acid, a sodium salt of polymethacrylic acid, an ammonium salt of polyacrylic acid and an ammonium salt of polymethacrylic acid. Thus, there may be up to 95% of the other powdered activator mixed with the powdered rubber, advantageously 5-95%, or preferably 25-75% based on the combined weight of the powdered rubber and the other activator.

In order that the invention may be more fully understood, reference is made to the accompanying drawings, wherein:

FIG. 1 shows a side elevational view of a section of hose or tubing which has a single slit parallel to the axis of the hose.

FIG. 2 shows a side elevational view of another section of hose or tubing with three slits parallel to the axis of the hose.

FIG. 3 is a schematic view of equipment for controlling the pressure and temperature for sealant testing.

In order to perform various tests on the efficiency of the sealant composition of this invention, the equipment shown in the drawings is used.

Fig. 1 shows a section of garden hose. Hose 1 has a slit 2 having a slit length of 1 inch (2.5 cm) running parallel to the axis of the hose. This slit is covered with a layer of alpha-cyanoacrylate 3 (commercial type Super Glue as marketed by Super Glue Corp.) with the layer of glue extending over an area of the tube adjacent to the slit.

Fig. 2 shows a section of Neoprene rubber hose having three such slits 1 with a spacing of 1 inch (2.5 cm) between adjacent slits in the tube with a layer of alpha-cyanoacrylate 3 covering the three slits and adjacent area.

Fig. 3 shows equipment for testing such tubing on which the layer has been cured by covering the alpha-cyanoacrylate layer with the powdered initiator (not shown) to effect curing and hardening of the cyanoacrylate to function as a sealant. Tank 6 is more than half filled with water 7. Pump 5 positioned between pipe or tubing 8 and pipe or tubing 8' is supported by plate 13'. Hose 1 is fastened by clamps 4 to join pipe 8' with pipe 8" which latter pipe is supported on plate 13. Plates 13 and 13' rest on supporting means which are not shown. Valve 10 is positioned on pipe 8" to control the flow of water therethrough. Catch pipe 11 catches water flowing out of pipe 8" and returns it to tank 6. Heater 12 is used to heat the water to desired temperatures so that the repaired hose can be operated under temperature and pressure conditions that the hose may be exposed to in actual use.

The invention is illustrated by the following Examples which are intended merely for purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it may be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

EXAMPLE I

A number of strips of alkyl alpha-cyanoacrylate (Super Glue) are laid out on a sheet of aluminium foil and a different powdered activator is applied to the surface of cyanoacrylate. The time of curing is noted in each case and after curing the strips are peeled off of the aluminum foil and compared for flexibility. The various activators, the time of cure and relative flexibility are reported in the following table.

TABLE I

Exp. No.	Powdered Rubber	Curing Time (Min)	Flexibility	
A.	Cis-1,4-Polyisoprene (Vulcanized & stabilized)	1-5	Most	5
B.	Butadiene-Acrylonitrile Copolymer (Hycar 1422)	1-5	Medium	10
B'.	Hycar 1411	1-5	Medium	
C.	Styrene-Butadiene Block Copolymer (Stabilized- Sol T-161)	3-10	Most	15
D.	Poly(chloroprene) "Neoprene WHV-A"	3-10	Medium	
E.	Cis-1,4-polybutadiene (No additives)	10-30	Medium	20
F.	1,2-Polybutadiene (No additives - Laboratory prepared)	10-30	Medium	
G.	Cis-1,4-polyisoprene (No additives)	10-30	Medium	25
H.	Poly(chloroprene) (No additives)	3-10	Medium	
I.	Poly-n-butyl-methacrylate (No additives)	3-10	Medium	30
Control	Alginate	1-5	Poor	

Particle size of the powdered rubber affects the flexibility, with fine particles giving better flexibility and large particles giving less flexibility. In all cases the flexibility with the various rubbers was improved over cyanoacrylate activated by polysaccharides such as alginate alone. However, the curing time and toughness are improved by incorporating 5, 25 and 50% by weight of a polysaccharide, such as alginate, guar gum, etc. with the powdered rubber. The addition of the polysaccharide does not appear to adversely affect strip flexibility.

EXAMPLE II

In a Neoprene fuel line hose having an inside diameter of 3/8 inch (9.5mm), three slits each one inch (2.5cm) long and one inch (2.5cm) apart as shown in Fig. 2 are cut into the hose as shown in Fig. 2. These slits together with the adjacent area extending about at least 1/4 inch (6.4mm) in all directions around the slits, are covered with a layer of alpha-cyanoacrylate (Super Glue). The hose is twisted to open the slits so as to allow the cyanoacrylate to wet the sides of the slits. Shortly thereafter the powdered rubber activator is applied to cover completely the layer of Super Glue. Then after about 10 minutes of curing, tests are performed with the equipment shown in Fig. 3. In order to raise the hose to the desired temperature the water in the tank 6 is heated to the desired temperature (about 22° C) and pumped through hose 1 until well heated. Then valve 10 is partially closed to maintain the desired pressure. When a leak develops in one of the slits, it is repaired with a layer of cyanoacrylate covered with a layer of powdered alginate to give a faster cure and then the test is continued to test the remaining repaired slits. The specific curing agent, the pressure applied, the water temperature and duration of tests are reported below in Table II.

TABLE II

Percent in Powder White Black Guar Rubber Rubber Gum	Number of Tubes With 3 Slits Each	Pressure Applied After Powder Cured (psi) (MPa)	No. of failures per Total No. of Slits	How Many Minutes Pressure Held Before Leak	Release
Control	1	80 .55	1/3	1	
A	1	80 .55	1/3	1	10 ^{*-3}
A'	1	80 .55	1/3	8	
B	1	50 .34	0	-	15
	1	80 .55	1/3	5	-
C	1	50 .34	0	-	5
	1	80 .55	0	-	15
	1	100 .69	0	-	5 ^{*-2}
D	1	50 .34	0	-	15
	1	80 .55	0	-	5
D'	1	50 .34	0	-	15
	1	80 .55	1/3	5	-
E	1	80 .55	1/3	5	-
E'	1	80 .55	0	-	15
F ^{*-4}	1	50 .34	0	-	15
	1	80 .55	0	-	5
G	1	80 .55	0	-	15
G'	1	80 .55	0	-	15

*-1 Polyisoprene rubber cut in small pieces (gives coarse powder) from polyisoprene rubber stopper

*-2 At 4.5 minutes the tube separated at 100 psi (.69MPa) but not at repaired ruptures.

*-3 After initial leak repaired, pressure applied and held for 10 minutes at 80 psi (.55MPa) before tube separated but not at repaired slits.

*-4 Test repeated three times with same results

*-5 White rubber is powdered Hycar 1422 produced by Goodrich.

EXAMPLE III

The procedure of Example II is repeated a number of times using the following combinations of powders individually to coat the cyanoacrylate:

- (a) 50% TP-20 and 50% Alginate
- (b) 50% TP-30 and 50% Alginate
- (c) 50% TP-40 and 50% Alginate
- (d) 75% TP-20 and 25% Guar Gum
- (e) 75% TP-30 and 25% Guar Gum
- (f) 75% TP-40 and 25% Guar Gum
- (g) 50% TP-20 and 50% Starch
- (h) 50% TP-30 and 50% Pectin
- (i) 50% TP-40 and 50% Gum Arabic

In each case there is no failure on any of the seals upon exposure to 50 psi (.34MPa) for 15 minutes and 80 psi (.55MPa) for 5 minutes.

EXAMPLE IV

The procedure of Example II is repeated using "Tygon" tubing having an inside diameter of 3/8 inch (9.5mm) (Tygon is the registered trademark of Goodrich Chemical Company for its polyvinyl chloride tubing).

Curing Agent	Applied Pressure	Water Temp. °C	Failure Time (Min.)
50% TP-20 50% Guar Gum	50 psi (.34MPa)	22	15

EXAMPLE V

A chromium plated copper tube having an inside diameter of 3/8 inch (9.5mm) has a 3/22 inch (3.5mm) hole drilled therein. This hole is covered with Super Glue and then with the activator combination of Example IV as described above following which testing in the equipment of Fig. 3 shows that the sealant withstands a pressure of 50 psi (.34MPa) at 22°C for 15 minutes.

EXAMPLE VI

The procedure of Example II is repeated a number of times with similar successful results using the activator combination of Example IV and as the alpha-cyanoacrylate the following respectively:

- (a) A 50-50 mixture of methyl and ethyl alpha-cyanoacrylate;
- (b) Butyl alpha-cyanoacrylate;
- (c) Hexyl alpha-cyanoacrylate;
- (d) Phenyl alpha-cyanoacrylate; and
- (e) Cyclohexyl alpha-cyanoacrylate.

The sealant of this invention can be used to seal openings of ruptures in any type of material. The only requirement is that the alpha-cyanoacrylate adheres effectively to the material.

The initiator material may be used in various mixtures with each other or with inert materials provided there is at least 25%, preferably at least 50% of the active ingredient or ingredients. The balance can be of various inert fillers or less active materials such as finely divided silica, graphite, etc.

Claims

1. A process for applying a sealant to a rupture or opening in a substrate, which comprises:
 - (a) applying a layer of an alpha-cyanoacrylate over the rupture or opening to be sealed and over the surface area adjacent to said rupture or opening, said alpha-cyanoacrylate being liquid at 20°C and having the formula $\text{CH}_2=\text{C}(\text{CN})\text{-COOR}$ wherein R is an aliphatic, aromatic or cycloaliphatic hydrocarbon group of up to 10 carbon atoms or an alkoxy, chloro or fluoro derivative of said hydrocarbon group in which any alkoxy group has from 1-4 carbon atoms therein; and
 - (b) spreading on said layer of alpha-cyanoacrylate a layer of a powder comprising rubber.
2. A process according to claim 1, in which R is an alkyl group of 1-6 carbon atoms.
3. A process according to claim 1 or 2, in which said powdered rubber is natural rubber, cis-1,4-polybutadiene, 1,2-polybutadiene, cis-1,4-polyisoprene, poly(chloroprene), butadiene-acrylonitrile copolymer, a random or block copolymer of styrene and butadiene, poly-(n-butyl-methacrylate) or a

terpolymer of butadiene, acrylonitrile and acrylic acid.

4. A process according to claim 1,2 or 3, in which said powdered rubber contains mixed intimately therein up to 95 percent by weight, preferably 25 to 75 percent by weight, of a powdered solid having hydroxyl and/or carboxylate groups therein.

5. A process according to claim 4, in which said powdered rubber contains from 25 to 75 percent by weight of said powdered solid having hydroxyl and/or carboxylate groups therein.

6. A process according to claim 4 or 5, in which said powdered solid is a monosaccharide or polysaccharide.

7. A process according to claim 4 or 5, in which said powdered solid is alginate, starch, pectin, carrageenan, locust bean gum, guar gum, cellulose, gum arabic, xanthate gum, sodium bicarbonate, polyvinyl alcohol, a vinylalcohol-vinylacetate copolymer having at least 25 percent by weight of vinylalcohol groups therein, a sodium salt of polyacrylic acid, a sodium salt of polymethacrylic acid, an ammonium salt of polyacrylic acid or an ammonium salt of polymethacrylic acid.

8. A process according to any of claims 1 to 7, in which a mixture of the methyl and ethyl esters of the alpha-cyanoacrylate is used.

9. A two-component sealant composition, each component being separately packaged prior to application, the first component (a) being an adhesive comprising a liquid alpha-cyanoacrylate having the formula $\text{CH}_2=\text{C}(\text{CN})\text{-COOR}$ wherein R is an aliphatic, aromatic or cycloaliphatic hydrocarbon group of up to 10 carbon atoms or an alkoxy, chloro or fluoro derivative of said hydrocarbon group in which alkoxy groups there are 1-4 carbon atoms; and the second component (b) being a solid powder comprising rubber.

10. A composition according to claim 9, wherein the said alpha-cyanoacrylate and/or the said solid powder comprising rubber are as defined in any of claims 2 to 8.

11. A sealant composition which comprises an alpha-cyanoacrylate adhesive in admixture with powdered rubber, the said alpha-cyanoacrylate having the formula $\text{CH}_2=\text{C}(\text{CN})\text{COOR}$ wherein R is an aliphatic, aromatic or cycloaliphatic hydro carbon group of up to 10 carbon atoms or an alkoxy, chloro or fluoro derivative of said group in which any alkoxy group has up to 4 carbon atoms.

12. A composition according to claim 11, wherein the alpha-cyanoacrylate and/or the powdered rubber are as defined in any of claims 2 to 8.

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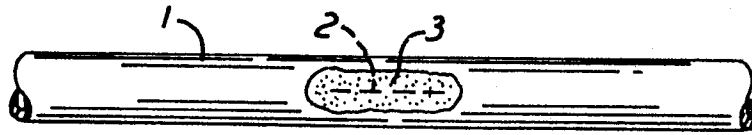


FIG. 1



FIG. 2

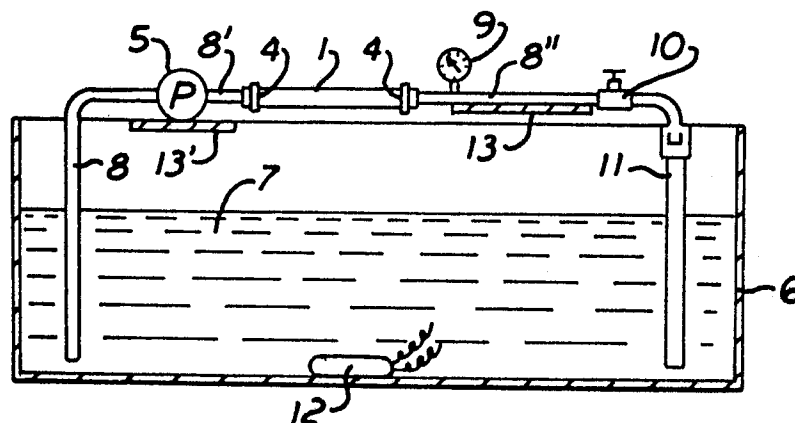


FIG. 3